ANALYSIS OF MEAD'S PATENTS

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Cathode Composition and Method for Solid State Lithium Battery. U.S. Patent # 4,576,883,
Mar 18, 1986. Henry F. Hope and Stephen F. Hope.

This patent describes the use of Li-Al alloys, formed by cathodic reduction of Al foil soaked in a lithium salt solution, as a means of reducing the large excess of lithium as the anode. Polymer electrolyte formed by milling heated polymer (e.g. polyethylene oxide) with crystals of the lithium salt to obtain uniform mixing, or via solvent-solute mixing followed by doctor blade casting directly on to the cathode. 25μm thick reproducible layers are possible.

The cathode comprise of a multiplicity of spheres, each sphere consist of a vanadium oxide core encapsulated in a polymer film. The polymer film consist of an inorganic salt and activated carbon. The V_6O_{13} was prepared by thermal decomposition of NH_4VO_3 with the resulting agglomerate size of 100-500μm powder ground further to reduce to several microns. The composite cathode was formed by emulsifying the V_6O_{13}, polymer, carbon and lithium salt in an organic solvent and casting via the doctor blade technique. The patent teaches that this kind of cathode construction have increased surface area, increased performance characteristics and increased active life in which the insertion compound is encapsulated in an electronically and ionically conducting polymeric material. The principal advantage of encapsulating the insertion compound in the polymeric sphere is a large increase in the available active surface area of the cathode. The insertion compound is also mechanically fixed which increases the active life of the cathode layer. They cited typical inorganic salts and polyethylene oxide as the polymer.

The whole process and claims made in the patent is common knowledge to everyone involved in polymer electrolyte battery work. Everything in the patent has appeared in the open literature. Although they do not refer to the early published work of Hooper and North (1983) which describes in some detail the operation of a polymer electrolyte battery, they do reiterate much of their work.

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Solid State Electrochemical Device. U. S. Patent # 4,638,407, Jan 20, 1987. Jorgen S. Lundsgaard.

An all-solid-state double layer capacitor and an all-solid state multi-cell electrochemical device utilizing ionically conducting polymer electrolytes are disclosed.

The background of the invention discusses the general layout of an electrochemical capacitor containing a liquid or paste electrolyte. The patent discloses plastic bonded V_6O_{13} - C structures (similar to U.S. Patent # 4,576,883) as composite cathode material. It discusses the concept of obtaining high surface area cathode via the patent of Hope et el, and utilizing them with polymer electrolytes in devices such as capacitors and multi-cell bipolar electrode stacks.

In my opinion the only originality to the patent is probably the use of two electronically conductive layers whereby both electrodes may be composite polymeric cathodes containing V_6O_{13}, electrolyte phase and carbon sandwiching the polymer electrolyte. However, the concepts of electrochemical capacitors and bipolar geometries are well known and understood from the open literature. So again the patent reiterates methods and issues that were published in journals before the patent filing date.

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Method For Preparing Encapsulated Cathode Material. U. S. Patent # 4,720,910, Jan 26, 1988.
John K. Rourke, Gerhart Schwab and Dale R. Shackle.

This patent describes the encapsulation of the insertion compound in an electronically and ionically conducting polymer using a spray drying technique.

The patent discusses solvent casting techniques described by North in a U.S. Patent # 4,589,197. Somehow they try to differentiate it with the U.S. Patent # 4,576,883 using encapsulation concept although that patent also involves solvent casting technique.

In this invention, insertion compounds are encapsulated by forming a dispersion of an insertion compound, an inorganic salt and a conductive material in a solution of a polymer in a volatile solvent and spray-drying the dispersion to evaporate the solvent and thereby form a particle in which the insertion compound is encapsulated as a core material in a polymeric shell containing the inorganic salt and conductive material. By using this cathode in solid state batteries, improved performance characteristics are exhibited. Alternatively, the carbon black can be admixed with spray-dried particles just as effectively.

The objective of the invention is to provide encapsulation of the insertion compound without agglomeration to yield more active cathode material whereby the polymer shell has both electronic and ionic conductivity. The patent cites typical insertion compounds but prefers V_6O_{13} or V_2O_5. The preferred polymer is polyethylene oxide and there is a whole range of preferred salts.

In grinding the insertion compound it is desirable to include some carbon, salt and polymer to prevent agglomeration of the insertion compound during or following the grinding process. The salt is believed to dissolve in the polymer.

The particle size of the cathode particles exiting from the spray-dryer is typically <3μm. This is controlled by adjusting slurry and air pressure in the atomizer.

The advantage of the polymer coated particles are the same as those cited by Hope et el.The patent describes several designs of polymer electrolyte batteries (vis-a`-vis, disc sandwiches, swiss-roll and concertinas) already available in the open literature. It then discusses that the encapsulated particles can be coated on to a current collector to forma cathode by dispersing the particles in a solution of a binder material such as PEO and coating this composition onto the current collector.(In this way one would expect the cathode composition to change since more PEO phase is being added and secondly the polymer shell encapsulating the V_6O_{13} should also dissolve in the solution instead of being dispersed.) So one effectively goes back to square one by emulsifying the V_6O_{13}, inorganic salt, carbon and polymer in a volatile organic solvent and coating onto the current collector.

Another method for forming the cathode involve coating the current collector with the dry encapsulated material and compressing to cause particles to fuse together and adhere to the substrates.

The grinding media in the attritor are steel balls. It is well known that iron contamination occurs in organic solvents. In my opinion the spray-drying technique of preparing the encapsulated cathode is very original. However, the rest of the patent is again open literature stuff.

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Solid State Electrochemical Device. U. S. Patent # 4,748,542, May 31, 1988. Jorgen S. Lundsgaard.

This patent is a continuation of U.S. Patent # 4,638,407, described earlier, again relating to a solid state capacitor. In this case the electrode composition consist only of carbon, PEO or any other ionically conducting polymer and inorganic salt (in U.S. patent # 4,638,407, V_6O_{13} was also the constituent). Only the concept of the plastic bonded electrode structure for capacitor application is described for both uni-polar and bi-polar cells. The bipolar electrode composition is extrusion coated on to the surface of the current collector and the electrolyte layer which is PEO combined with the inorganic salt is coated on to the electrode layer by either extrusion or solvent cast technique.

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Liquid Coating Polymer Networks as Solid Electrolytes. U. S. Patent # 4,792,504, Dec 20,1988.
Gerhart Schwab, Mei-Tsu Lee.

This patent describes polymer electrolytes consisting of cross-linked polyethylene oxide complexed with a metal salt and a dipolar aprotic solvent.

The background of the invention discusses some of the early problems encountered with ionically conducting polymeric electrolytes. Attempts to increase the mechanical strength was usually made at the expense in the ionic conductivity and vice-versa.

An earlier patent by Bauer et al (U.S. Patent # 4,654,279) describes a solid polymeric electrolyte which is a two phase interpenetrated network of a mechanically supporting phase of a continuous network of a cross-linked polymer and an ionically conducting phase comprising of a metal salt and a liquid polymer such as liquid polyethylene oxides (glycols?). Representative examples of the mechanically supporting phase include epoxies, polyurethanes, polyacrylates, polymethacrylates, polystyrenes and polyacrylonitriles.

The present patent uses cross-linked PEO as the mechanically supporting phase and a metal salt dissolved in an aprotic solvent. The PEO continuous phase is preferably cross-linked using a polyacrylate cross-linking agent (cross-linking agents described in U.S.Patent # 3,734,876). The polyacrylate is reacted with PEO in an amount of 3-6 parts per 100 parts PEO. A free radical catalyst is also required. The preferred solvents are dimethyl ethers of glycols such as PEGDME.

The concept of this patent is the same as Bauer et al. The only exception is that different materials are used. Chemical cross-linking is described.

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Electrode Construction for Solid State Electrochemical Cell. U.S.Patent # 4,808,496, Feb 28, 1989. Henry F. Hope and Stephen F. Hope.

Reiterates the U.S. Patent #s 4,576,883 and 4,720,910 with very little additions to the patent. A few extra representation of salts have been included. The patent recommends polymeric encapsulation of the lithium electrode using a spray-drying technique and depositing on to an Al substrate as described earlier for the cathode electrode layer.

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Radiation Cured Solid Electrolyte and Electrochemical Devices Employing the Same. U.S. Patent # 4,830,939, May 16, 1989. Mei-Tsu Lee, Dale Shackle and Gerhart Schwab.

This patent describes a method for forming an interpenetrating polymeric network containing a liquid electrolyte. The mixture consist of a liquid monomeric or prepolymeric radiation prepolymerizable compound, a radiation inert ionically conducting liquid and an alkaline metal salt. The radiation is actinic to crosslink the polymerizable ionically conducting material and form a solid matrix for the ionically conducting liquid.

The distinction made with the earlier U.S. patent (# 4,792,504) is that U.V. or electron beam radiation is used here to crosslink the polymer.

The patent describes a method of fabricating anode and cathode half-elements (e.g. Li anode coated with radiation polymerizable electrolyte which is subsequently polymerized to protect underlying anode material). The cathode is made by coating a composite mixture consisting of the appropriate materials on to a current collector and subjecting to actinic radiation.

Alternatively, a cured anode or cathode half element may be assembled with an uncured anode or cathode half element and the assembly subjected to radiation to adhere the two elements together. In another method uncured anode and cathode half elements are assembled together and radiation cured after assembly.

Polyethylenically unsaturated monomeric or prepolymonomerics are preferred. Examples include reacting a polyethylene glycol with acrylic or methacrylic acid. The radiation curable polymers such as polyethylene glycol-300 diacrylate have molecular weights 200-800 and are liquids at less than 30°C. It is desirable to include radiation curable comonomer such as tetrahydrofurfuryl acrylate in the composition to reduce tg and improve ionic conductivity of the polymer. The radiation inert liquid can be any low volatile aprotic solvents such as propylene carbonate having a boiling point greater than 80°C. The amount of radiation curable polymer and inert liquid is adjusted to yield optimum strength and optimum conductivity.

The anode and cathode half elements are the same as described earlier. The cathode material is dispersed in the radiation curable composition before polymerization. The various form of coatings are described in some detail. Numerous claims are also disclosed on the electrochemical cell fabrication. In my opinion this is probably the most complete patent so far screened.

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